



# Roles of lattice oxygen in V<sub>2</sub>O<sub>5</sub> and activated coke in SO<sub>2</sub> removal over coke-supported V<sub>2</sub>O<sub>5</sub> catalysts

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## Abstract

This paper systematically investigates the roles of lattice oxygen in V<sub>2</sub>O<sub>5</sub> and activated coke over coke-supported V<sub>2</sub>O<sub>5</sub> catalysts in SO<sub>2</sub> removal process at 200 °C. The results show that one SO<sub>2</sub> molecule reacts with one O atom in a surface V<sub>2</sub>O<sub>5</sub> molecule to form an intermediate (a VOSO<sub>4</sub>-like structure), which then reacts with gaseous O<sub>2</sub> to form sulfur species (SO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> in the presence of H<sub>2</sub>O) and V<sub>2</sub>O<sub>5</sub>. The SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> migrates over the coke surface and stores in the pores in the vicinity of V<sub>2</sub>O<sub>5</sub> sites. Mineral matters, oxygen and nitrogen species in the activated coke are unfavorable to migration of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. The pores effective for storage of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> are those less than 1 nm in size.

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## 1. Introduction

SO<sub>2</sub> and NO in flue gas are major air pollutants and must be removed before emission. Among various emission control technologies [1–3], activated coke (AC) and activated carbon fiber (ACF) were found to have good SO<sub>2</sub> removal activities at temperatures below 100 °C [3–8]. However, flue gases are usually maintained at temperatures around 150 °C or higher for self-ventilation. This makes the use of AC/ACF-based technologies difficult because flue gases must be cooled down for SO<sub>2</sub> removal and then be heated up for ventilation.

Our recent work [9,10] found that supporting V<sub>2</sub>O<sub>5</sub> onto an AC (V<sub>2</sub>O<sub>5</sub>/AC) results in high activities in SO<sub>2</sub> removal as well as in selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> at temperatures around 200 °C. This V<sub>2</sub>O<sub>5</sub>/AC-based technology not only allows flue gas self-ventilation, but also solves NO pollution simultaneously. Studies regarding SCR reaction over

V<sub>2</sub>O<sub>5</sub>/AC have been reported in our earlier works [11,12]; SO<sub>2</sub> removal over V<sub>2</sub>O<sub>5</sub>/AC is studied in detail in this paper.

The SO<sub>2</sub> removal process over porous carbon materials was found involving a number of steps: adsorption of SO<sub>2</sub>, oxidation of SO<sub>2</sub> to SO<sub>3</sub>, reaction of SO<sub>3</sub> with H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub>, and storage of H<sub>2</sub>SO<sub>4</sub> in pores [4,13,14]. Surface oxygen groups were found to be important for absorption and oxidation of SO<sub>2</sub> [13,15], and surface area and pore volume were important for absorption of SO<sub>2</sub> and storage of H<sub>2</sub>SO<sub>4</sub> [4,16,17]. Since storage of H<sub>2</sub>SO<sub>4</sub> or SO<sub>3</sub> in the pores decreases SO<sub>2</sub> removal activity, the SO<sub>2</sub>-captured catalyst/sorbent has to be regenerated at a certain conversion level by water washing or reductive decomposition to recover its activity.

SO<sub>2</sub> removal over V<sub>2</sub>O<sub>5</sub>/AC consists of two steps: removal and regeneration. The mechanism proposed for SO<sub>2</sub> removal was [9]:

- (1) adsorption of SO<sub>2</sub> on V<sub>2</sub>O<sub>5</sub> sites or on AC sites adjacent to V<sub>2</sub>O<sub>5</sub> sites;
- (2) activation of SO<sub>2</sub> by V<sub>2</sub>O<sub>5</sub> to form a VOSO<sub>4</sub>-like intermediate;
- (3) reaction of the VOSO<sub>4</sub>-like intermediate with O<sub>2</sub> to form SO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>;

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(4) migration of  $\text{SO}_3$  over the surface, reaction of  $\text{SO}_3$  with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$ , and storage of  $\text{H}_2\text{SO}_4$  in the pores of AC.

Apparently,  $\text{SO}_2$  removal mechanism of  $\text{V}_2\text{O}_5/\text{AC}$  is different from that of  $\text{AC}/\text{ACF}$  in catalytic oxidation of  $\text{SO}_2$ . In the absence of  $\text{V}_2\text{O}_5$ , oxygen functional groups on  $\text{AC}/\text{ACF}$  are responsible for  $\text{SO}_2$  oxidation, which is effective at temperatures below 100 °C. However, in the presence of  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$  is responsible for  $\text{SO}_2$  oxidation, especially at temperatures around 200 °C. In addition to the role of  $\text{V}_2\text{O}_5$ , the higher  $\text{SO}_2$  removal activities of  $\text{V}_2\text{O}_5/\text{AC}$  should also be related to the properties of AC since poor  $\text{SO}_2$  removal activity was found for  $\text{V}_2\text{O}_5$  supported on other materials. In this regard, it is interesting to quantify the effects of  $\text{V}_2\text{O}_5$  and AC on  $\text{SO}_2$  removal at around 200 °C. This information is of importance for validating catalytic mechanism of  $\text{V}_2\text{O}_5/\text{AC}$ .

## 2. Experimental

### 2.1. Preparation of catalysts

A coal-derived coke (a commercial product of Xinhua Chemical Company, Taiyuan, China) is used as the raw material. The coke is activated in steam at 850 °C for 40, 60, 80, 120 and 160 min to yield a variety of ACs with different surface textures. These ACs are named AC40, AC60, AC80, AC120 and AC160 according to the activation time. To eliminate possible influence of minerals (ash), all the AC samples are subjected to acid wash at 60 °C for 12 h using an aqueous solution containing 2 mol/l HCl and 2 mol/l HF. The demineralized AC samples (with ash contents <0.6%) are marked with a prefix DM-. To introduce oxygen functional groups to AC's surface, DM-AC80 is treated with an aqueous  $\text{HNO}_3$  solution (2 mol/l) at 60 °C for 12 h and then washed with distilled water to neutral and dried at 110 °C for 5 h. The resulting sample is named NDM-AC80.

The  $\text{V}_2\text{O}_5/\text{AC}$  catalysts are prepared by pore volume impregnation of the AC supports with an aqueous solution containing ammonium metavanadate and oxalic acid. The catalysts are then dried at 50 °C for 5 h and at 110 °C overnight and subsequently calcined in  $\text{N}_2$  at 500 °C for 5 h and then exposed in air at 250 °C for 5 h. The catalysts are named according to their components. V2/(DM-AC80) refers to DM-AC80 supported with 2 wt.%  $\text{V}_2\text{O}_5$ , for example.

### 2.2. Activity measurement

A fixed bed reactor is used for  $\text{SO}_2$  removal experiment. The feed contains 1600 ppm  $\text{SO}_2$ , 500 ppm NO, 4.5%  $\text{O}_2$ , 2.5%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$  and 500 ppm  $\text{NH}_3$ . It should be pointed out that 500 ppm NO is introduced into the feed to simulate flue gas and 500 ppm  $\text{NH}_3$  is to reduce NO. Our previous work [9] found that NO and  $\text{NH}_3$  in the feed do not influence  $\text{SO}_2$  removal over  $\text{V}_2\text{O}_5/\text{AC}$ . Therefore,  $\text{SO}_2$  removal behavior is investigated in the presence of NO and  $\text{NH}_3$ .

To identify the different roles of  $\text{O}_2$  and the lattice oxygen of  $\text{V}_2\text{O}_5$  in  $\text{SO}_2$  removal,  $\text{O}_2$ -response experiments were

Table 1  
BET surface area and pore volume of the catalysts

Catalyst	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Pore volume (<1 nm) (cm <sup>3</sup> /g)
V2/(DM-AC40)	306	0.13	0.09
V2/(DM-AC60)	405	0.19	0.12
V2/(DM-AC80)	621	0.26	0.16
V2/(DM-AC120)	700	0.27	0.15
V2/(DM-AC160)	496	0.26	0.12
V2/AC80	609	0.28	0.17
V2/(NDM-AC80)	631	0.28	0.16

performed in the fix bed reactor. The feed contains 500 ppm  $\text{SO}_2$ , 4.5%  $\text{O}_2$  (when used), 2.5%  $\text{H}_2\text{O}$  and balance  $\text{N}_2$ . All the experiments are made at 200 °C with 3 g catalysts and a total flow of 400 ml/min, corresponding to a space velocity of 8000 l/kg h.  $\text{SO}_2$ , NO and  $\text{O}_2$  concentrations of the feed and the effluent are measured on line by a flue gas analyzer (Drager, Germany).

### 2.3. Characterizations of physical and chemical properties

BET surface area and pore volume of the  $\text{V}_2\text{O}_5/\text{AC}$  samples are determined by  $\text{N}_2$  adsorption at 77 K using a surface analyzer (ASAP2000, Micromeritics). Pore size distribution is calculated based on Density Functional Theory (DFT). BET surface area and pore volume of the catalysts are shown in Table 1.

X-ray diffraction (XRD) pattern of the  $\text{V}_2\text{O}_5/\text{AC}$  samples are obtained on a Rigaku computer-controlled D/max 2500X using  $\text{Cu K}\alpha$  as the radiation source. The applied current and voltage are 30 mA and 40 kV, respectively.

C, H, O, N and S contents in ACs are measured on an element analyzer (Vario EL, Germany). It should be pointed out that O content in ACs is the amount of surface oxygen and the amount of lattice oxygen can be estimated according to  $\text{V}_2\text{O}_5$  loading (5 lattice oxygen in 1  $\text{V}_2\text{O}_5$  molecule). Results show that the former is higher than 2.3 wt.% and the latter is no more than 0.9 wt.%.

Mineral matter characterization was carried out according to GB/T 1574-1995 method designated for analysis of ash composition of coals.

## 3. Results and discussion

### 3.1. The role of lattice oxygen in $\text{V}_2\text{O}_5$ in $\text{SO}_2$ removal

Fig. 1 shows  $\text{SO}_2$  removal behavior of DM-AC80 supported with different amounts of  $\text{V}_2\text{O}_5$ .  $\text{SO}_2$  removal activity of the support DM-AC80 is very low, but the activity increases greatly with an increase in  $\text{V}_2\text{O}_5$  loading. This indicates the importance of  $\text{V}_2\text{O}_5$  in  $\text{SO}_2$  removal, although the amount of lattice oxygen in  $\text{V}_2\text{O}_5$ , no more than 0.9 wt.% (V2/(DM-AC80)), is much lower than that of surface oxygen, 2.75 wt.%.

In our previous work [9], it was found that an adsorption peak of  $\text{VOSO}_4$  was observable on the used  $\text{V}_2\text{O}_5/\text{AC}$  through Fourier transformed infrared spectroscopy (FTIR) and dis-

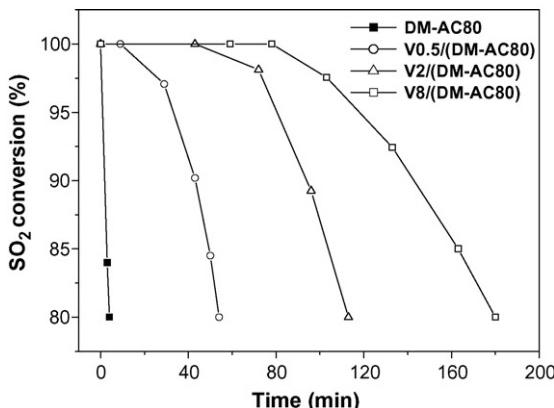


Fig. 1. SO<sub>2</sub> conversions of DM-AC80-supported V<sub>2</sub>O<sub>5</sub> catalysts. Reaction conditions: 1600 ppm SO<sub>2</sub>; 500 ppm NO; 500 ppm NH<sub>3</sub>; 4.5% O<sub>2</sub>; 2.5% H<sub>2</sub>O; 200 °C.

appeared after exposition to an O<sub>2</sub> + H<sub>2</sub>O environment at 200 °C. These suggest that V<sub>2</sub>O<sub>5</sub> chemically absorbs SO<sub>2</sub> to form a VOSO<sub>4</sub>-like intermediate firstly, and then the intermediate reacts with O<sub>2</sub> to form SO<sub>3</sub> [9]. To differentiate the effect of these two steps on SO<sub>2</sub> removal activity, O<sub>2</sub>-response experiments are carried out in this work, where O<sub>2</sub> is removed from the feed at a time on stream of 5 min and then resumed at a SO<sub>2</sub> conversion of 60%. The removal of O<sub>2</sub> aims to terminate reactions between the VOSO<sub>4</sub>-like intermediate and O<sub>2</sub>, and to evaluate the amount of intermediate formed. The results in Fig. 2 show that SO<sub>2</sub> conversion of DM-AC80 drops quickly before the O<sub>2</sub> interruption while SO<sub>2</sub> conversions of all the V<sub>2</sub>O<sub>5</sub>-loaded DM-AC80 catalysts maintain at 100% for some time after the O<sub>2</sub> interruption (this time is defined as breakthrough time). Additionally, a higher V<sub>2</sub>O<sub>5</sub> loading results in a longer breakthrough time and a slower decrease in SO<sub>2</sub> conversion after the SO<sub>2</sub> breakthrough. When O<sub>2</sub> is resumed to the feed, SO<sub>2</sub> conversions of all V<sub>2</sub>O<sub>5</sub>-loaded samples rise to 100% at the same rate, regardless of the differences in V<sub>2</sub>O<sub>5</sub> loading or the amounts of VOSO<sub>4</sub>-like intermediate formed. These data indicate that the reaction between the VOSO<sub>4</sub>-like intermediate and gaseous O<sub>2</sub> is very fast and does not limit the overall SO<sub>2</sub> removal process under the conditions used. In other words, the formation rate of VOSO<sub>4</sub>-like intermediate is the limiting step, which is influenced by V<sub>2</sub>O<sub>5</sub> loading.

It is reasonable to believe that lattice oxygen in V<sub>2</sub>O<sub>5</sub> is responsible for the formation of VOSO<sub>4</sub>-like intermediate. The amount of lattice oxygen involved in the intermediate formation at each V<sub>2</sub>O<sub>5</sub> loading can be estimated from the amount of SO<sub>2</sub> adsorbed during the O<sub>2</sub>-interruption, which is determined by extrapolation of the decreasing SO<sub>2</sub> conversion after the breakthrough to the horizontal axis (the dash lines in Fig. 2) and integration of the area under the SO<sub>2</sub> conversion curve. Since the amount of residual O<sub>2</sub> in the system after the O<sub>2</sub>-interruption is small (at a space velocity of 8000 l/kg h) and the support DM-AC80 absorbs little SO<sub>2</sub> after the O<sub>2</sub>-interruption, the amount of SO<sub>2</sub> determined from the integration (in mole, termed  $\delta\text{SO}_2$ ) corresponds to the amount of lattice oxygen used for the formation of VOSO<sub>4</sub>-like

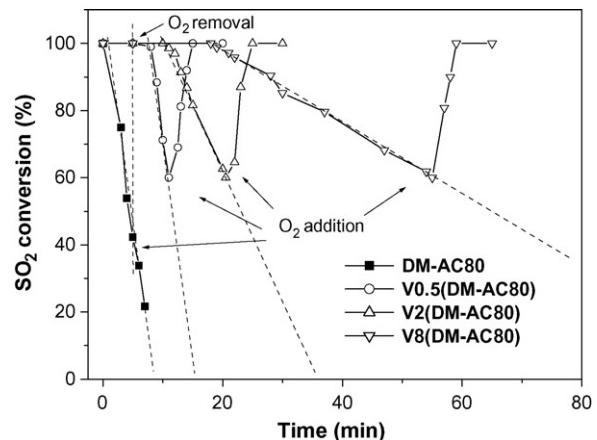


Fig. 2. O<sub>2</sub>-response experiments during SO<sub>2</sub> removal over DM-AC80-supported V<sub>2</sub>O<sub>5</sub> catalysts. Reaction conditions: 500 ppm SO<sub>2</sub>; 2.5% H<sub>2</sub>O; 4.5% O<sub>2</sub> (when used); 200 °C.

intermediate. This type of lattice oxygen is termed “effective lattice oxygen” (ELO in short) to distinguish them from all the oxygen in V<sub>2</sub>O<sub>5</sub>. If one SO<sub>2</sub> molecule combines one ELO atom in the intermediate formation, the amount of ELO equals  $\delta\text{SO}_2$  (in mole). Fig. 3 shows the amount of ELO determined for the three V<sub>2</sub>O<sub>5</sub>-loaded catalysts (solid squares). If one V<sub>2</sub>O<sub>5</sub> molecule provides one ELO atom, a straight line can also be obtained (the dash line in Fig. 3). Apparently, the amount of ELO increases with an increase in V<sub>2</sub>O<sub>5</sub> loading. In addition, the amount of ELO at a low V<sub>2</sub>O<sub>5</sub> loading of  $2.8 \times 10^{-5}$  mol/g (0.5 wt.%) is very close to the dash line while those at higher V<sub>2</sub>O<sub>5</sub> loadings are far from the dash line. These may indicate that the highest usage of O atom in a V<sub>2</sub>O<sub>5</sub> molecule is about one, but the O usability decreases with increasing V<sub>2</sub>O<sub>5</sub> loading. This is understandable because a lower V<sub>2</sub>O<sub>5</sub> loading may result in finer dispersion of V<sub>2</sub>O<sub>5</sub> on AC while a higher V<sub>2</sub>O<sub>5</sub> loading usually results in more agglomerated V<sub>2</sub>O<sub>5</sub> particles and relatively less surface V<sub>2</sub>O<sub>5</sub>. To show the difference in particle size of V<sub>2</sub>O<sub>5</sub>, XRD analyses were performed. However, there are no diffraction peaks of V<sub>2</sub>O<sub>5</sub> for all the samples and no valuable information can be obtained.

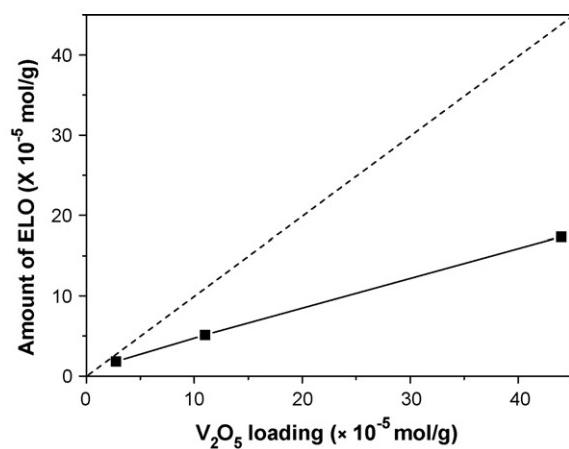


Fig. 3. Amount of effective lattice oxygen (ELO) vs. V<sub>2</sub>O<sub>5</sub> loading over DM-AC80.

The information obtained so far indicates that one surface  $\text{V}_2\text{O}_5$  molecule provides one ELO atom, which adsorbs and oxidizes one  $\text{SO}_2$  molecule to form one  $\text{VOSO}_4$ -like intermediate. In this process, the valence of V changes from  $\text{V}^{5+}$  to  $\text{V}^{4+}$ , which is consistent with the XPS analysis reported by Ma et al. for the same type of catalyst [10].

### 3.2. Usability of ACs' pores and its relation with $\text{V}_2\text{O}_5$

Since the role of  $\text{V}_2\text{O}_5$  on  $\text{SO}_2$  removal is to provide lattice O to oxidize  $\text{SO}_2$  to a  $\text{VOSO}_4$ -like intermediate, the differences in  $\text{V}_2\text{O}_5$  loading affect only the rate of  $\text{SO}_2$  oxidation. However, the data in Fig. 1 show that the rate of  $\text{SO}_2$  oxidation is high enough for all the  $\text{V}_2\text{O}_5$ -loaded catalysts because their initial  $\text{SO}_2$  conversions are all 100%. This suggests that the different  $\text{SO}_2$  removal behavior of the  $\text{V}_2\text{O}_5$ -loaded catalysts results from other factors. According to the proposed  $\text{SO}_2$  removal mechanism reported by Ma et al. [10], the  $\text{SO}_3/\text{H}_2\text{SO}_4$  storage capacity of AC is a possible factor.

It is logical to believe that not all the pores in the AC is usable for storage of  $\text{SO}_3/\text{H}_2\text{SO}_4$ , and only the pores in the vicinity of  $\text{V}_2\text{O}_5$  sites are able to accept and store  $\text{SO}_3/\text{H}_2\text{SO}_4$  migrated from  $\text{V}_2\text{O}_5$  sites. A lower  $\text{V}_2\text{O}_5$  loading yields fewer and smaller  $\text{V}_2\text{O}_5$  sites and thus fewer pores for storage of  $\text{SO}_3/\text{H}_2\text{SO}_4$  and therefore a lower  $\text{SO}_2$  removal activity. A higher  $\text{V}_2\text{O}_5$  loading yields more and possibly larger  $\text{V}_2\text{O}_5$  sites, and thus more pores to be accessible for storage of  $\text{SO}_3/\text{H}_2\text{SO}_4$ . It is worth to note that at higher  $\text{V}_2\text{O}_5$  loadings, some of the pores in the vicinity of one  $\text{V}_2\text{O}_5$  site may be close to other  $\text{V}_2\text{O}_5$  sites. This hypothesis is shown in Fig. 4.

To estimate the pore usability of AC in  $\text{SO}_2$  removal process, the volumes of  $\text{H}_2\text{SO}_4$  stored, termed “effective pore volume” or EPV in short, are calculated by subtracting the amounts of  $\text{SO}_2$  combined with ELO from corresponding  $\text{SO}_2$  capacities. The  $\text{SO}_2$  capacities, termed  $\Delta\text{SO}_2$ , are determined from Fig. 1 as the areas between  $\text{SO}_2$  conversion curves of  $\text{V}_2\text{O}_5$ -loaded catalysts and that of the support (DM-AC80). Fig. 5 shows that EPV increases with an increase in  $\text{V}_2\text{O}_5$  loading but the values are small, even much smaller than the volume of pores with diameters less than 1 nm. This phenomenon agrees with the hypothesis in Fig. 4.

The discussions presented so far show that the role of  $\text{V}_2\text{O}_5$  in  $\text{V}_2\text{O}_5/\text{AC}$  in  $\text{SO}_2$  removal is to provide lattice O for  $\text{SO}_2$  oxidation, and to serve as a center for distribution of  $\text{SO}_3/\text{H}_2\text{SO}_4$  to the AC's pores in its vicinity. To show these roles more clearly, the catalyst-mass-based parameters ELO, EPV and  $\Delta\text{SO}_2$  presented above are divided by the loading of  $\text{V}_2\text{O}_5$  (in mole)

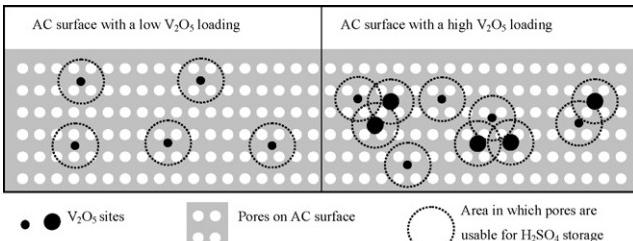


Fig. 4. Hypothetic mapping of  $\text{V}_2\text{O}_5/\text{AC}$  catalyst surface.

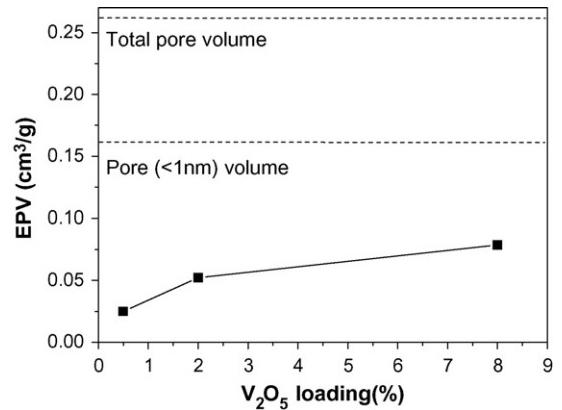


Fig. 5. Effective pore volume (EPV) of the catalysts vs.  $\text{V}_2\text{O}_5$  loading.

in the catalysts, and the results are shown in Fig. 6. The values of  $\text{ELO}/\text{V}_2\text{O}_5$ ,  $\text{EPV}/\text{V}_2\text{O}_5$  and  $\Delta\text{SO}_2/\text{V}_2\text{O}_5$  all decrease with an increase in  $\text{V}_2\text{O}_5$  loading, but the decreases in  $\text{EPV}/\text{V}_2\text{O}_5$  and  $\Delta\text{SO}_2/\text{V}_2\text{O}_5$  are relatively faster than that in  $\text{ELO}/\text{V}_2\text{O}_5$ . This indicates that  $\text{V}_2\text{O}_5$  sites preferentially locate at certain parts of AC surface, resulting in less increase in EPV in comparison to an increase in ELO when  $\text{V}_2\text{O}_5$  loading is increased. This is also demonstrated by the ratios of  $\text{EPV}/\text{ELO}$ , which are 1330, 990 and 530  $\text{cm}^3/\text{mol}$  for V0.5/(DM-AC80), V2/(DM-AC80) and V8/(DM-AC80), respectively. All these information indicate that the decrease in  $\text{SO}_2$  conversion in the later stage of  $\text{SO}_2$  removal as shown in Fig. 1 is influenced mainly by the EPV, which is affected by the distribution of  $\text{V}_2\text{O}_5$  on the AC surface.

### 3.3. Effects of ACs' physical and chemical properties on EPV

It is important to note that EPV is still a superficial parameter of AC. It may depend not only on volume of pores available for  $\text{H}_2\text{SO}_4$  storage but also on surface properties which possibly influences migration of  $\text{SO}_3/\text{H}_2\text{SO}_4$  from  $\text{V}_2\text{O}_5$  sites to nearby pores.

#### 3.3.1. Effects of ACs' physical properties on EPV

Fig. 7 shows  $\text{SO}_2$  removal behavior of various  $\text{V}_2\text{O}_5/\text{AC}$  catalysts with 2 wt.%  $\text{V}_2\text{O}_5$  but different AC supports. As

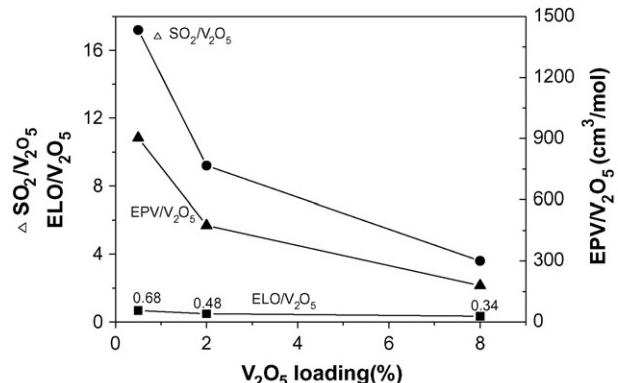


Fig. 6. Mole ratio of  $\text{ELO}/\text{V}_2\text{O}_5$ ,  $\Delta\text{SO}_2/\text{V}_2\text{O}_5$  and  $\text{EPV}/\text{V}_2\text{O}_5$  vs.  $\text{V}_2\text{O}_5$  loading on DM-AC80.

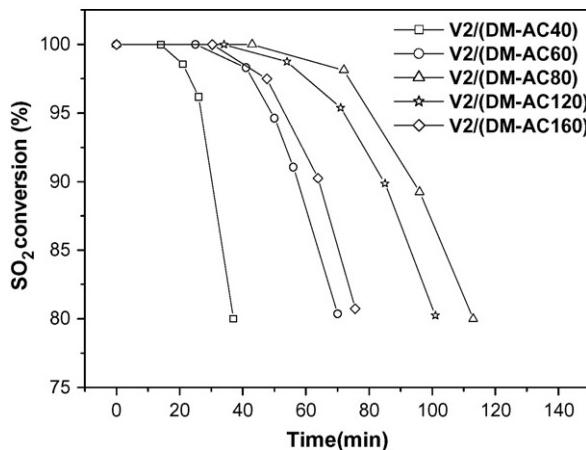


Fig. 7.  $\text{SO}_2$  conversions of the catalysts with 2 wt.%  $\text{V}_2\text{O}_5$  but different ACs. Reaction conditions: 1600 ppm  $\text{SO}_2$ ; 500 ppm  $\text{NO}$ ; 500 ppm  $\text{NH}_3$ ; 4.5%  $\text{O}_2$ ; 2.5%  $\text{H}_2\text{O}$ ; 200 °C.

stated in the experimental section, these AC supports were made from the same coke but subjected to steam activation at 850 °C for different periods of time, which ensures that the differences of ACs are mainly in pore texture. The results in Fig. 7 apparently indicate that the  $\text{SO}_2$  removal capacity increases with an increase in steam activation time from 40 to 80 min, but then decreases with a further increase in steam activation time to 160 min. To see whether the amount of ELO changes with the steam activation time,  $\text{O}_2$ -response experiments are performed on V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120) and the results are shown in Fig. 8. As expected, the three catalysts show the same behavior, indicating the same amount of ELO. This indicates that the steam activation time of AC has little effect on distribution of  $\text{V}_2\text{O}_5$  and the different  $\text{SO}_2$  behaviors in Fig. 7 can be attributed mainly to the difference in EPV.

Fig. 9a shows the relations of EPV determined from Fig. 7 and physical properties of the catalysts with activation time. Among the four curves, the changes in EPV seem correlating well only with the changes in volume of pores smaller than 1 nm. This is understandable because  $\text{H}_2\text{SO}_4$  is mainly stored in

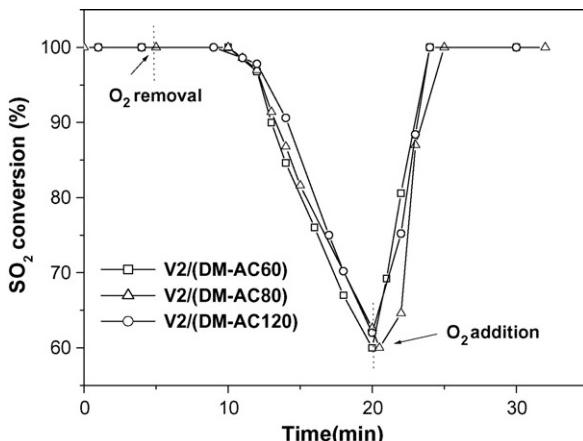


Fig. 8.  $\text{O}_2$ -response experiments during  $\text{SO}_2$  removal over V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120). Reaction conditions: 500 ppm  $\text{SO}_2$ ; 2.5%  $\text{H}_2\text{O}$ ; 4.5%  $\text{O}_2$  (when used); 200 °C.

the micro-pores as reported in the literature [4,18]. Fig. 9b correlates EPV with volume of pores smaller than 1 nm for all the catalysts with 2 wt.%  $\text{V}_2\text{O}_5$ . It is clear that the data of the catalysts with DM-AC as supports form a straight line, indicating a strong relation between EPV and pores smaller than 1 nm.

The significant deviations for V2/AC80 (not subjected to the de-mineralization treatment) and V2/(NDM-AC80) (subjected to a  $\text{HNO}_3$  treatment after the de-mineralization treatment) from the straight line indicate that chemical properties also affect the value of EPV.

### 3.3.2. ACs' chemical properties and its relation with EPV

Fig. 10a shows  $\text{SO}_2$  conversion behaviors of V2/AC80, V2/(DM-AC80) and V2/(NDM-AC80) as well as that of the supports. The supports themselves (filled symbols) show little  $\text{SO}_2$  removal capacity, but they do make significant differences in  $\text{SO}_2$  removal behavior when 2 wt.%  $\text{V}_2\text{O}_5$  is loaded onto them (open symbols). Compared to V2/AC80, the de-mineralized support increases the  $\text{SO}_2$  removal capacity (see V2/(DM-AC80)) but a further  $\text{HNO}_3$  treatment decreases the  $\text{SO}_2$  removal capacity (see V2/(NDM-AC80)). To see whether the differences in AC supports affect ELO,  $\text{O}_2$ -response experiments are performed on these  $\text{V}_2\text{O}_5$ -loaded catalysts. The results in Fig. 10b shows similar amounts of ELO for the three catalysts, which indicates again that the differences in  $\text{SO}_2$  removal behaviors of the catalysts result

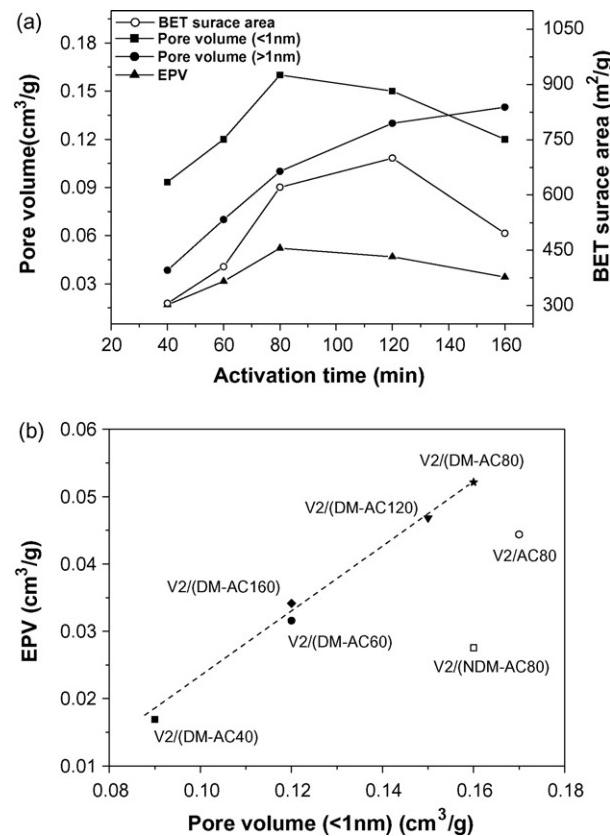


Fig. 9. (a) BET surface area, pore volume and EPV vs. activation time; (b) EPV vs. pore volume (<1 nm).

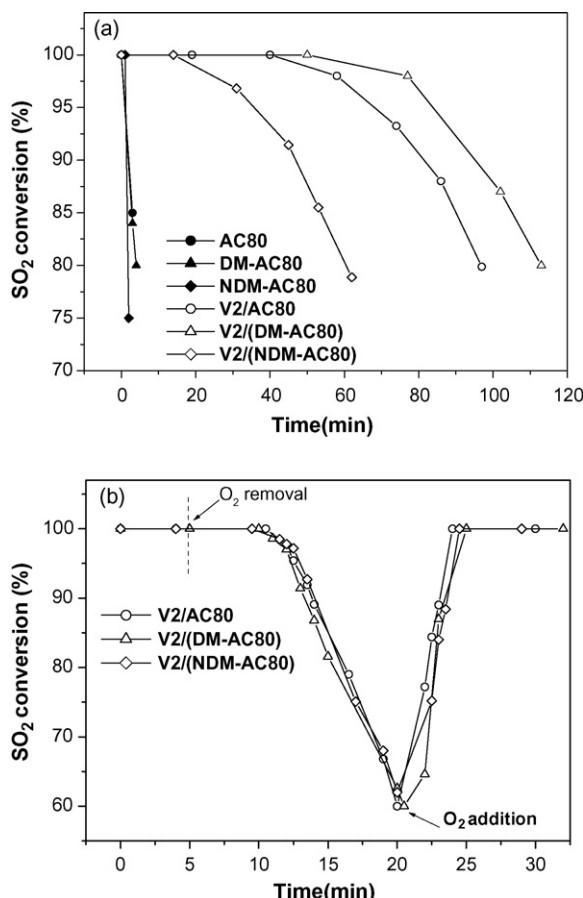


Fig. 10. Effect of AC treatments on SO<sub>2</sub> removal. (a) SO<sub>2</sub> conversions at 200 °C; reaction conditions: 1600 ppm SO<sub>2</sub>; 500 ppm NO; 500 ppm NH<sub>3</sub>; 4.5% O<sub>2</sub>; 2.5% H<sub>2</sub>O and (b) O<sub>2</sub>-response experiment; reaction conditions: 500 ppm SO<sub>2</sub>; 2.5% H<sub>2</sub>O, 4.5% O<sub>2</sub> (when used); 200 °C.

from the differences in EPV of the AC supports. Since these AC supports show similar physical properties (see Table 1), their differences should mainly be attributed to differences in chemical properties. Table 2 shows that the demineralization of AC80 results in a significant reduction in ash content, from 8.2% to 0.25%, but not in the contents of other elements (see AC80 and DM-AC80). Treatment of DM-AC80 with HNO<sub>3</sub> results in significant increases in O and N contents, from 2.75% to 5.85% and from 0.79% to 1.50%, respectively, but little changes in contents of other compo-

Table 2  
Elemental and ash analyses of the different activated cokes (wt.%)<sup>a</sup>

Sample	C	H	O <sup>b</sup>	N	S	Ash
DM-AC40	94.87	0.71	2.64	0.64	0.56	0.58
DM-AC60	95.58	0.61	2.31	0.60	0.57	0.33
DM-AC80	94.99	0.68	2.75	0.79	0.54	0.25
DM-AC120	94.34	0.79	3.01	0.86	0.54	0.46
DM-AC160	95.26	0.52	2.54	0.68	0.61	0.39
AC80	87.36	0.59	2.56	0.74	0.55	8.20
NDM-AC80	91.20	0.69	5.85	1.50	0.54	0.22

<sup>a</sup> Moisture-free basis.

<sup>b</sup> By difference.

nents. These data suggest that the minerals, O-containing and N-containing functional groups in AC prevent migration of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. This finding indicates that oxygen functional groups play different roles in SO<sub>2</sub> removal at different temperatures.

#### 4. Conclusions

Compared to activated cokes (AC), V<sub>2</sub>O<sub>5</sub>/AC are more active for SO<sub>2</sub> removal from flue gases at temperatures around 200 °C. The role of V<sub>2</sub>O<sub>5</sub> is to provide lattice oxygen to absorb and oxidize SO<sub>2</sub> into a VOSO<sub>4</sub>-like intermediate. The intermediate then reacts with gaseous O<sub>2</sub> to form SO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. The amount of lattice oxygen in V<sub>2</sub>O<sub>5</sub> used for the intermediate formation (this type of lattice oxygen is termed ELO) is dependent on the V<sub>2</sub>O<sub>5</sub> loading and independent of the properties of AC support under the conditions used. The maximum amount of ELO is one atom per V<sub>2</sub>O<sub>5</sub> molecule at low V<sub>2</sub>O<sub>5</sub> loadings.

The role of AC is to store the SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> from V<sub>2</sub>O<sub>5</sub> sites. Only the pores in the vicinity of V<sub>2</sub>O<sub>5</sub> sites are available for storage of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. The volume of these pores, termed EPV, is influenced by the physical properties of AC support, which is proportional to but significantly smaller than the volume of pores smaller than 1 nm. The EPV is also influenced by the chemical properties of AC support. Minerals, O-containing and N-containing functional groups in AC may inhibit migration of SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>.

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